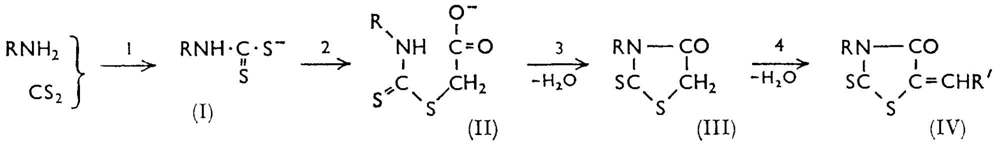
946. *The Synthesis of Some New Derivatives of Rhodanine*

By W. I. Stephen and A. Townshend

New rhodanine derivatives, including interesting pyridine derivatives, have been prepared during an investigation of such compounds as analytical reagents.[1] The general method of synthesis [2,3] was followed by condensation with *p*-dimethylaminobenzaldehyde.[4] The 3-substituted rhodanines (III) were readily prepared, but, instead of 3-(2-pyridyl)-rhodanine, compound (II; R = 2-pyridyl) [5] was formed under our reaction conditions. We found, however, that the dehydrating conditions used in the aldehyde condensation also close the ring, so that the 3,5-disubstituted rhodanine is produced in good yield by reaction of the non-cyclised compound with the aldehyde.



Reagents: 1, base; 2, $ClCH_2\cdot CO_2^-$; 3, conc. HCl; 4, R′CHO.

When ethylenediamine is used, 1,2-di-(3-rhodanyl)ethane is produced.[6] It has been possible to isolate the 5-mono- and 5,5-di-4-dimethylaminobenzylidene derivatives of this compound. The species described by Nägele,[6] m. p. 212°, was probably a mixture of these two compounds.

The new compounds are described in the Table.

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[1] A. Townsend, Ph.D. Thesis, Birmingham University, 1963.
[2] A. Miolati, *Annalen*, 1891, **262**, 82.
[3] J. von Braun, *Ber.*, 1902, **35**, 3368.
[4] N. Campbell and J. E. McKail, *J.*, 1948, 1251.
[5] E. B. Knott, *J.*, 1956, 1644.
[6] H. Nägele, *Monatsh.*, 1912, **33**, 941.

			Found (%)			Reqd. (%)		
Compound	Ref.	M. p.	C	H	S	C	H	S
3-(2-Picolyl)rhodanine	*a*	100—101°	47·9	4·0	28·8	48·2	3·6	28·6
3-(4-Picolyl)rhodanine	*b*	149—150	47·9	4·0	—	48·2	3·6	—
3-*Substituted* 5(4-*dimethylaminobenzylidene*)*rhodanines*								
3-*p*-Dimethylaminophenyl	*c*	260—261	62·6	5·8	17·1	62·5	5·5	16·7
3-n-Propyl	*d*	134·5—135	58·7	6·0	21·1	58·8	5·9	20·7
3-(2-Pyridyl)	*e*	238·5—239·5	59·75	4·8	18·4	59·8	4·4	18·8
3-(2-Picolyl)	*f*	204·5—205	61·0	5·1	17·8	60·8	4·8	18·0
3-(4-Picolyl)	*g*	207—207·5	60·7	5·5	18·3	60·8	4·8	18·0
1,2-*Diaminoethane derivatives*								
1-[5(4-Dimethylaminobenzylidene)-3-rhodanyl]-2-(3-rhodanyl)-	*h*	179—180	48·1	3·7	28·9	48·2	4·0	30·3
1,2-Di-[5-(4-dimethylaminobenzylidene)-3-rhodanyl]-	*i*	304·5 (decomp.)	55·4	4·9	23·4	56·3	4·7	23·1

a, Colourless plates (78%) (from aqueous ethanol). *b*, Yellow-brown plates (93%) (from aqueous ethanol). *c*, Red crystals (from ethanol–acetone). *d*, Red needles (from acetone). *e*, Deep red crystals (from acetone). *f*, Shimmering red needles (from ethanol–benzene). *g*, Pale red leaves (from acetone). *h*, Bright red powder. *i*, Dark red crystals, insoluble in the common organic solvents.

Experimental.—3-(2-*Picolyl*)*rhodanine* (III; R = 2-pic). 2-Picolylamine (21·7 g., 0·2 mole) was dissolved in a mixture of ethanol (20 ml.) and carbon tetrachloride (20 ml.). Carbon disulphide (23 ml., 0·38 mole) was added slowly, with water-cooling. Carbon tetrachloride (20 ml.) was added, the suspension allowed to stand for 2 min., and the precipitate filtered off, washed, and dried, to give (27·1 g., 92%) of 2-picolylammonium 2-picolyldithiocarbamate.

Sodium chloroacetate (25·6 g., 0·22 mole) was dissolved in water (60 ml.) and neutralised with sodium carbonate. This solution was heated to 35°, and kept at this temperature while the dithiocarbamate was added in 1-g. amounts, with continuous stirring. The resulting solution was poured slowly into boiling, concentrated hydrochloric acid (75 ml.), which was boiled for a further 15 min. The white suspension produced was neutralised with concentrated aqueous ammonia. The yellow oil that formed solidified on cooling; further crystallisation also occurred. All solids were filtered off, ground up, and washed well with water. More ammonia was added to the combined filtrate and washings until no more precipitate was obtained. This was treated in the same way as the main yield and combined with it; the total yield of colourless crystals was 16·2 g. (78%); they were recrystallised from aqueous ethanol. The other 3-substituted rhodanines were prepared similarly.

N-(2-*Pyridyl*)*thiocarbamoylthioglycollic acid*. The dithiocarbamate was prepared by the method of Fairfull and Peak [7] and condensed with chloroacetate as above. The product was lime-coloured crystals, m. p. 126—127° (lit.,[5] 133°).

Condensations with p-*dimethylaminobenzaldehyde*. These were carried out according to the general procedure of Campbell and McKail.[4] 1-[5-(4-Dimethylaminobenzylidene)-3-rhodanyl]-2-(3-rhodanyl)ethane was separated from 1,2-di-[5-(4-dimethylaminobenzylidene)-3-rhodanyl]-ethane by Soxhlet extraction with acetone, unreacted aldehyde being removed by subsequent extraction of the product with aqueous 4N-hydrochloric acid.

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[7] A. E. S. Fairfull and D. A. Peak, *J.*, 1955, 796.